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Cement Microstructure: Fostering Photocatalysis

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Abstract

The singularities and the qualities of the hydrated cement microstructure have been identified by researchers as enhancers to promote photocatalytic processes, mediated by titanium dioxide, to create environment-friendly cement. In this chapter, we intend to expose the microstructural characteristics of cement and those aspects that make it possible for the promotion of photocatalytic activity. Within the inherent complexity of the cement microstructure, we describe a framework of two key elements in the microstructure of this material that affects the promotion of TiO_2 photocatalysis, to offer a more comprehensive view of the physical-chemical processes involved. These elements are: the porosity and the nanostructure of the C-S-H. This framework is also a starting point for future studies that seek to improve the photocatalytic response of titanium dioxide inserted in the cement matrix, as well as to provide implications for the application of photocatalytic cement technology in the construction materials industry.

Keywords: titanium dioxide, photocatalysis, cement porosity, calcium-silicate-hydrate (C-S-H), photodegradation, photocatalytic cement

1. Introduction

Cement develops its microstructure during its hydration process, which is, without any doubt, one of the most studied phenomena in materials science. Its high complexity is due to the number of actors involved in the process as well as the conditions in which it is being developed. Several physical-chemical processes take place in a perfectly coordinated manner, resulting in a material with exceptional properties. Cement clinker reacts with water giving insoluble hydration products which, in a cement paste (a mixture of cement powder and water) or concrete (a cement paste containing sand and aggregate filler), gradually replace the water in the

spaces between the cement grains and aggregate particles, and eventually provide a matrix that effectively binds the composite mass together. The reaction products, called hydrates, are responsible for strength development and they give cement its binding properties.

The hardening reaction in a cement paste is mainly associated with the hydration of the two calcium silicate compounds which occupy more than 80% by mass of the anhydrous clinker of ordinary Portland cement. These two phases produce the same products when they react with water: on the one hand, a colloidal calcium silicate hydrate, also known as a C-S-H gel, is formed together with a crystalline solid solution of calcium hydroxide, Ca(OH)_2 or CH, also called portlandite, which tends to form large crystals with a distinctive hexagonal-prism morphology. Within a few hours of mixing with water, cement paste starts to gain in stiffness and strength, going from a viscous fluid to a plastic solid, and finally, to a stiff solid. This change occurs because the hydration products have a lower density than the anhydrous phases and occupy more space, filling most of the space created by the consumption of water and increasing the solid volume. There are two main steps involved: the rapid initial formation of gelatinous hydrate coatings around the cement grains and, after a dormant period, the growth from these coatings of fibrillar C-S-H gel material into a reticulate network between the cement grains. **Figure 1A** and **B** show two scanning electron micrographs of Portland cement pastes. **Figure 1A** illustrates early hydration of the paste, where amorphous-looking gelatinous envelope of C-S-H gel bridges the cement grains at their points of contact. CH portlandite can also be observed among micro and macroporous structure of the hydrated material. **Figure 1B** corresponds to a mature paste, where C-S-H gel shows a fibrous morphology, which provides a reticular network within the system. C-S-H is then considered as responsible for the cement paste's internal skeleton, for the paste's adherence to the aggregates in the formation of mortar and concrete and for the strength and durability of cement-based materials.

This complex microuniverse has been explored by scientists for decades and even more since the recent developments of nanotechnology. The new and powerful tools for visualization, manipulation, and analysis of nanostructures have made it possible to host nanomaterials in the cement microstructure, providing the material with novel properties, or consolidating or improving its most characteristic behavior. In this sense, nanotechnology has allowed interesting developments which include the use of nanoparticles, carbon nanotubes, nanofibers and latest generation of additives to improve the strength and durability of cement-based materials

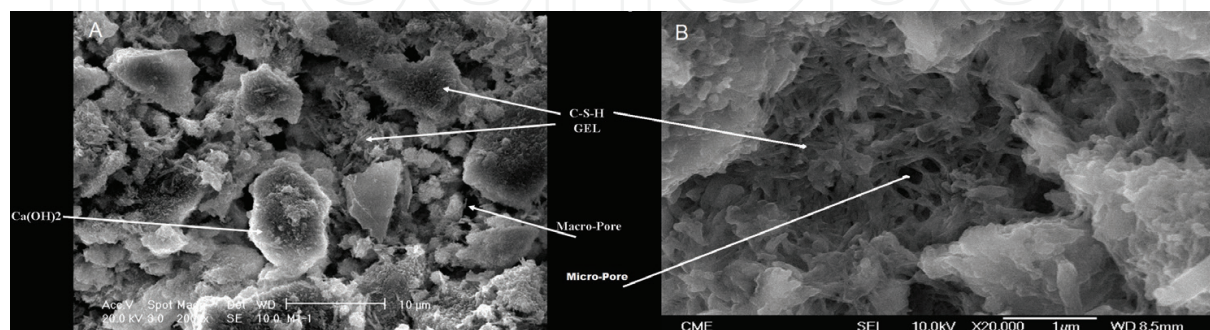


Figure 1. Scanning electron micrograph of hydrated Portland cement, (A) at early stage of hydration, and (B) fibrillar C-S-H gel in mature Portland cement paste.

[1–3]. Of special interest for building materials is nano-titanium dioxide. Its photocatalytic characteristics provide additional functionality mainly used to remove organic contaminants from surfaces exposed to ultraviolet radiation, such as road pavements and cement-based facade finishing products [4]. In addition, it has been proven that TiO_2 nanoparticles accelerate the hydration rate and increase the degree of hydration of the cement matrix [5].

This growing interest that has appeared in recent years by the nanoscale, is derived from the fact that the properties of the same material vary, and even new ones appear, depending on the size. This is the case with titanium dioxide, a semiconductor formed by covalent bond between titanium metal and oxygen. Titanium, the ninth most common element in the earth's crust, is a metal that is found in nature but not in a free form. Titanium interacts naturally with oxygen to form titanium oxides, which are commonly found in minerals, powders, sands and soils. The beginnings of the TiO_2 industry go back 30 years when paint manufacturers were looking for a substitute for white lead, which is considered toxic. It was then when it caught the attention of the entire scientific community, to verify the important positive characteristics that it has: it is chemically stable, non-toxic and inexpensive. On the other hand, the increase of the specific surface that occurs when this semiconductor is in the form of nanoparticles gives it greater functionality to promote reactions that take place on the surface, such as photocatalytic processes. Titanium dioxide as a nanomaterial can be found in several crystalline phases, the most common being anatase, brookite, and rutile. The first two are transformed to rutile with the increase in temperature, since the latter is the most thermodynamically stable under normal conditions. Anatase and rutile have an octahedral structure, while brookite has an orthorhombic system.

In this chapter, we intend to expose the microstructural aspects of hydrated cement that promote photocatalytic processes based on titanium dioxide. Initially, the physical mechanisms that give photocatalytic properties to TiO_2 in the form of nanoparticles will be detailed. Next, the microstructural characteristics of the cement-base materials modified with titanium dioxide nanoparticles will be described, analyzing their feasibility as new construction materials. Consequently, we describe a framework of two key elements in the microstructure of this material that affect the promotion of TiO_2 photocatalysis, to offer a more comprehensive view of the physical-chemical processes involved. These elements are: the porosity and the nanostructure of the C-S-H gel. At the end, several possible routes are suggested for future investigations in heterogeneous photocatalysis in cement.

2. TiO_2 -driven heterogeneous photocatalysis

Heterogeneous photocatalysis is a physical-chemical process that occurs in certain semiconductors when they are excited by electromagnetic radiation of a certain wavelength. The photocatalytic reaction begins when an incident photon promotes an electron from the valence band (VB) to the conduction band (CB), provided that the energy absorbed from the photon is equal to or greater than the semiconductor gap, leaving behind a hole in the valence band. The electron-hole pair produced catalyzes oxidation reactions of certain organic compounds adsorbed on the surface of the semiconductor, such as the NO_x pollutant, in the presence of

water molecules. Electrically, titanium dioxide is a wide-band-gap semiconductor (3 eV for rutile and 3.2 eV for anatase), requiring photons of wavelength less than 383 nm and greater than 403 nm respectively to promote valence band electrons.

Four chain reactions are fundamentally involved in the overall process: (1) photoexcitation: transfer of energy from a photon to an electron producing an electron–hole pair, (2) adsorption of organic species on the surface of the semiconductor, (3) capture and recombination of charge carriers and (4) interfacial load transfer. These four mechanisms compete with a possible electron–hole recombination. **Figure 2** illustrates the process of TiO_2 -driven heterogeneous photocatalysis of NO_x species.

The effectiveness of the photoinduced reactions is controlled by the light absorption characteristics of the semiconductor, which in turn depend on (1) the microstructural characteristics of the semiconductor itself, (2) the energy of the incident photons and (3) the substrate where the reactions take place. As for the semiconductor microstructure, it would be desirable for it to have a series of important properties:

- high specific surface;
- uniform distribution of particle size;
- spherical particles; and
- presence of superficial defects that promote the adsorption reactions of contaminating species.

In this regard, TiO_2 has been successfully nanostructured in the form of nanoparticles by a variety of techniques and a wide range of sources. Due to its greater surface area, porosity and number of defects and its photochemical reactivity, the catalytic performance obtained from TiO_2 nanoparticles is significantly improved compared to that obtained if the material was not nanostructured. On the other hand, it is necessary that the photocatalyst process is triggered

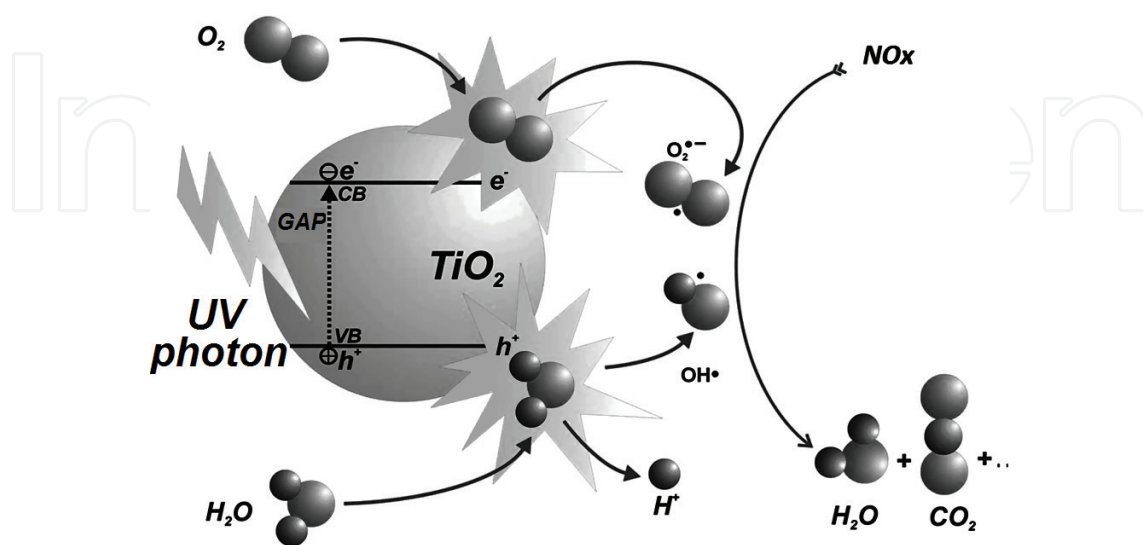


Figure 2. Heterogeneous photocatalysis of titanium dioxide for NO_x degradation: photoexcitation of an electron from the semiconductor valence band to the conduction band, leaving a positive hole in the valence band.

by photons belonging to the spectrum of ultraviolet radiation, which can be obtained from solar radiation. This aspect, together with the excellent properties of TiO_2 as a photocatalyst, results in a clearly versatile and low-cost degradation technology for air pollutants.

Despite these proven functional characteristics, such as self-cleaning, antimicrobial properties as well as the degradation of a range of organic (e.g., volatile organic compounds) and inorganic pollutants (e.g., NO_x and SO_2), technical aspects such as UV radiation acquiring, are still a limitation for the large-scale application of this light-driven technology [6]. In addition, the photocatalysis mechanism of TiO_2 has certain limitations that hinder the development of commercial applications, for example, the large band gap of TiO_2 , the electron-hole recombination process and deactivation of TiO_2 by partially oxidized intermediate blocks that occupy active catalytic sites on the photocatalyst.

3. Influence of nanosized TiO_2 on cement hydration

The incorporation of nano- TiO_2 as a filler in a cementitious matrix presents distinctive microstructural characteristics. Research has shown that the photocatalytic activity is superior in nano-crystalline TiO_2 and that it exhibits maximum efficiency in anatase phase compared to rutile or brookite phase [7]. When added to Portland cement, it is considered to act as inert filler and has not been believed to take part in the hydraulic reaction of Portland cement. However, the modification of particle size distribution due to chemically inert filler addition changes the system porosity, providing additional sites for nucleation of cement hydration products; consequently, the kinetics reaction might be catalyzed. In this sense, Jayapalan et al. [8] reported an increasing effect in the rate of early age hydration proportional to the dosage of TiO_2 , as well as found that smaller particles seem to accelerate the reaction more than larger particles. While in this and other reported studies TiO_2 particles were added as TiO_2 nanopowder and mixed with water prior to the addition of cement, researchers have recently been investigating the effects on the microstructure and photocatalytic activity of cement pastes doped with nanosized TiO_2 prepared by other techniques; as, for example, sol-gel method [9].

Consequently, relevant research on this topic concludes in the same consequences that come from housing TiO_2 nanoparticles on the cement microstructure. On the one hand, the nanoparticles are located in the porous structure of the cement and promote the formation of C-S-H gel around, forming microspheres that are interconnected by fibrillar structures of C-S-H (**Figure 3A and B**). On the other hand, the nanoparticles of TiO_2 present in the cement matrix decrease the pore size and promote the formation of hydration products through the consumption of capillary water displaced from the pores. As observed in **Figure 3**, the TiO_2 nanoparticles are covered with inner C-S-H gel. Most of the nanoparticles preferentially cluster at the entrance of the micropores, which may reasonably increase the overall density and promote the formation of C-S-H inside these micropores. These findings, widely confirmed by many researchers, point out that TiO_2 nanoparticles present in the cement matrix accelerate C-S-H gel formation and improve the microstructure of cementitious materials by shifting the distributed pores to finer ones.

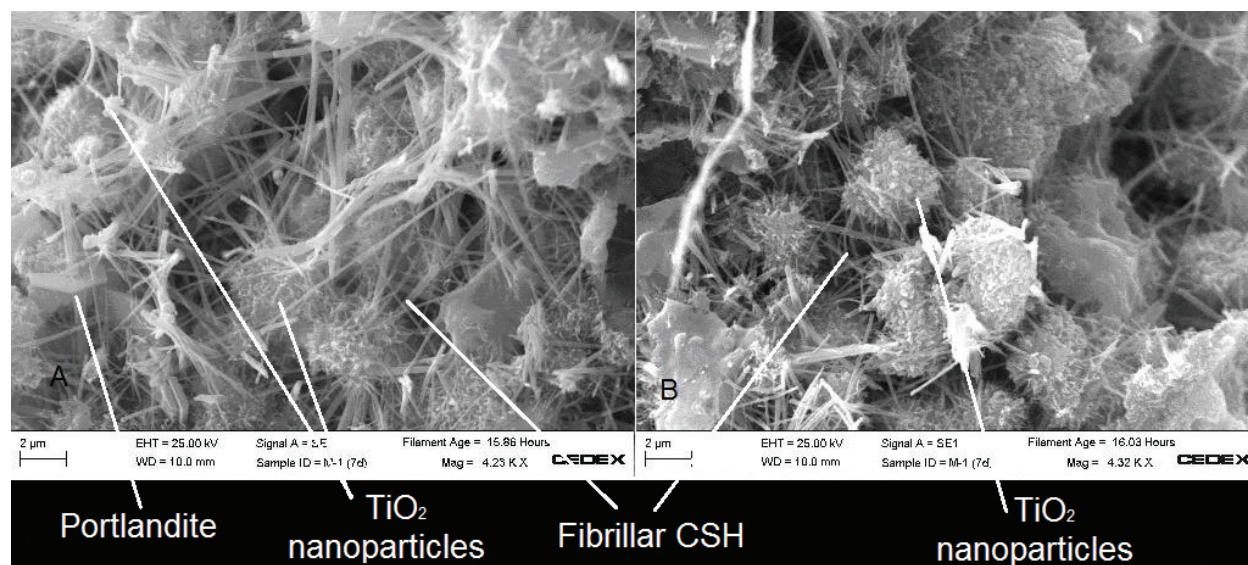


Figure 3. (A) Detail of SEM micrograph of TiO_2 -doped cement paste after 7 days hydration time, showing shell microspheres of amorphous inner C-S-H gel formed around the TiO_2 nanoparticles. Fibrillar outer C-S-H bridges the spheres filling the inter-hydrate space. (B) Same TiO_2 -cement paste after 14 days hydration displaying the same features.

4. Fostering photocatalysis through cement microstructure

In the previous section, we have exposed the most significant effects that nanoparticles of titanium dioxide, as filler, cause on the microstructure of the hydrated cement. Extensive research has been reported to show these clear modifications in the microstructure: decrease of porosity, increase of density in the C-S-H gel and increase of hydration products in the cement matrix. However, there exist not many works dedicated to the study of the cement microstructure as a valid support to favor the processes of photocatalysis. In this section, we try to explore the most relevant microstructural characteristics of hydrated cement for the promotion of the photocatalytic activity of nano- TiO_2 .

The first view of the problem indicates that in order to obtain reasonable rates of photocatalytic activity, the substrate must be able to adsorb the pollutant particles and trap them in some way to expose them to the photocatalytic process. The adsorption of contaminants on the surface of the photocatalyst is, therefore, an important factor in achieving high rates of degradation. To promote adsorption, composite structures comprising inert domains coexisting with photocatalytic domains can be used. In this way, the pollutants are adsorbed first in the inert sites and then diffuse to the photocatalytic domains. This is the so-called “Adsorb and Shuttle” (A&S) effect [10]. In this sense, there are important benefits derived from the use of the microstructure of the cement matrix as a suitable substrate for the nano- TiO_2 photocatalyst. The TiO_2 nanoparticles are located in the porous microstructure of the cement, where surface and volume irregularities occur. This defects population also promotes the adsorption of inorganic species that are trapped on the surface. On the other hand, since the water molecules participate in the photocatalytic process both as adsorbents, as OH sources and as reaction products, it is obvious that the water content that naturally possesses the cementitious materials can have a significant effect on photocatalytic efficiency.

It is evident then that the porosity and the presence of water of hydration in the microstructure of the cement are influential factors in the photocatalytic activity. With the aim to deeply analyze these factors, we propose a framework that helps identify the conditions for potential photocatalysis substrates in the cement material. Porosity and nanostructure of C-S-H gel are the two key elements in the microstructure of this material that affect the promotion of TiO_2 photocatalysis and will be studied in the following subsections.

4.1. Pore system of cement microstructure

When cement particles are dissolved and surrounded by water, they can react to produce solid reaction products (surface products) or spontaneously nucleate in the capillary water to produce crystals (pore products) [11]. The surface product is mainly the C-S-H gel and the major pore product is portlandite (CH). Yet, the surface product (C-S-H) is still porous media at nanoscale, forming gel pores, thus small molecules can diffuse through, and generally, its surfaces are negatively charged. In **Figure 4**, the presence of surface products (C-S-H, labeled as (1)) and pore products (portlandite crystals, labeled as (2)), can be observed in the microstructure, which occupy different spots, leaving spare room in between them. These voids are macropores (pore size larger than $50\ \mu\text{m}$), which are normally filled by water vapor. The capillary pores, however, are voids with average radius ranging from 5 to $5000\ \text{nm}$, where water persists even after hydration in completed, and that were previously available for pore products' nucleation.

This landscape draws a complex porous structure whose pore size distribution can vary from nanometers to thousands of microns, if macropores due to inadequate compaction are also

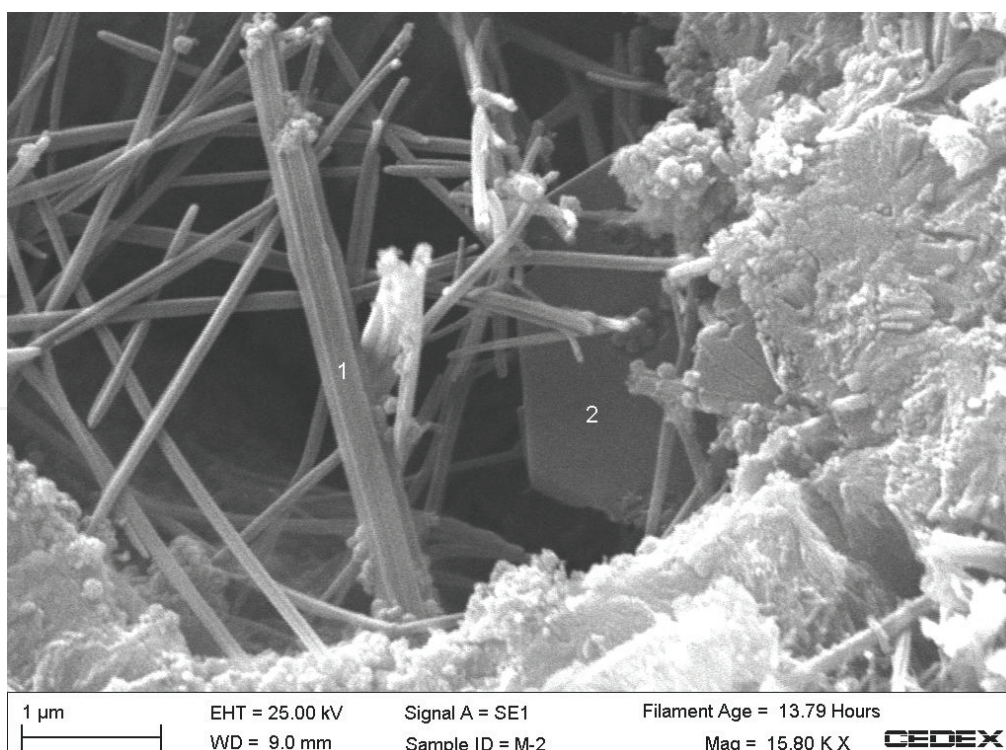


Figure 4. Scanning electron micrograph of cement paste displaying (1) C-S-H gel and (2) portlandite crystals as surface product and pore product respectively.

present. Moreover, large pores could be connected to gel pores through the fine capillary pores. Cement porosity is therefore directly related to the water present in the mix. The classification of the state of water in cement paste is generally based on the location where it is held and the nature of its bonding with the solid structure. Apart from the water vapor in the pores and the capillary water, it is suggested that water can also exist as adsorbed water (held by hydrogen bonds on the surface of the hydrated particles) and interlayer water [12]. Thus, the inherent availability of water in the vicinity of capillary pores leads to consider these porous structures as possible inert domains for hosting the photocatalytic nanoparticles.

4.2. Nanostructure of C-S-H gel

Since the C-S-H gel is the main solid reaction product that is formed during the hydration process, its presence must necessarily be compatible with the nanoparticle housing. As we have seen, nanoparticles not only do not interact negatively with the gel, but they are able to promote its development; therefore, the nanostructure of the C-S-H must be a clear reference in the photocatalytic capacity of TiO_2 .

Hydrated cement is a continually evolving material: even after the hydration process has reached its end, the material keeps experiencing changes due to both increased hydration of the cement particles and changes in the microstructure of the products after they form. These changes include increases in the specific surface area, changes to the pore size distribution and a continued increase in stiffness. Likewise, the evolution of the C-S-H gel during hydration time implies changes in its density. Therefore, understanding the formation of the gel nanostructure is crucial to predict its mass/volume ratio.

Among the many different structural models suggested for C-S-H, the colloidal models proposed by Jennings [13] successfully explain various bulk properties of C-S-H found in hydrated cement pastes. The basic of these models is the existence of a 5-nm-diameter building block. These basic units pack together to form the microstructure of C-S-H. However, more recent studies [14] propose that the basic building block is a unit of C-S-H that is roughly spherical and approximately 2 nm across with a specific surface area of about 1000 m^2/g . These building blocks flocculate to form larger units. This model has been already validated by many experimental works [15], where spherical nanostructures of C-S-H gel have been found. According to this model, the density of the smallest unit that can be used to build the nanometer structure of C-S-H is taken as 2450 or 2800 kg/m^3 , which are typical of the values for densities reported in the literature. Taking into account the high density of the C-S-H basic unit, the probability of a nanoparticle falling within a volume close to the gel is reasonable. Furthermore, according to this model, water fills the pore space starting with the finest, which impulses the idea of placing the TiO_2 nanoparticles in capillary pores that might be directly connected or closely near to fine deposits of water.

4.3. Cement as substrate-mediator for TiO_2 photocatalysis

Before discussing the validity of cement microstructure as support for photocatalysis of nano- TiO_2 , let us expand the implications of the photoinduced reactions that take place during photocatalysis. Once the UV photon has promoted the electron to the conduction band, leaving a gap in the valence band, this electron-hole pair is “trapped” and should proceed with the interfacial charge transfer process to directly oxidize/reduce contaminants or generate reactive oxidants.

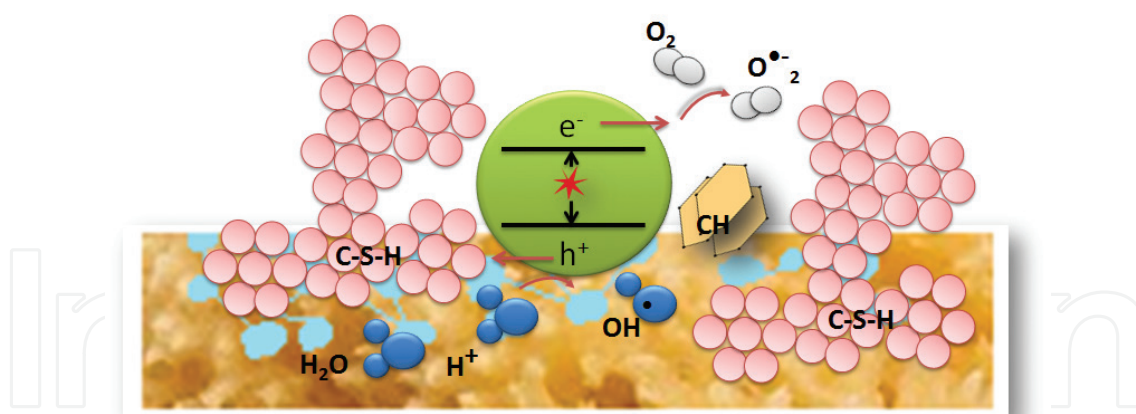


Figure 5. Illustration of cement-mediated charge recombination on nano-TiO₂ in the photocatalysis conversion process.

The transfers of trapped electrons and trapped holes should be fast enough to compete against electron-hole recombination, which is the main process that limits the overall photocatalysis performance. All this occurs on the surface of TiO₂; therefore, the charge transfer reactions are clearly limited by the photocatalyst surface conditions.

In the cement microstructure, the TiO₂ nanoparticles are naturally placed in the capillary pores, since these locations are surrounded by vapor water and are thermally stable. In this situation, the nanoparticles exhibit high surface specific area and have defects around them that act as traps for the adsorbents. Moreover, the capillary pores are connected to each other by capillary water, which ensures the provision of water molecules essential for the photocatalytic process to take place.

In this picture, we now add the presence of C-S-H gel nanostructures as nanosphere clusters, in addition to portlandite crystals that prefer to nucleate in the surface pores. We must remember that the density of the C-S-H gel is very high, and it is also surrounded by negative charge. On the other hand portlandite, namely calcium hydroxide, tends to react with oxygen and carbon dioxide to form calcite. These facts ensure the presence of molecular oxygen in the vicinity of nano-TiO₂. The situation is illustrated in **Figure 5**.

Owing to the negative charges of the C-S-H gel nanostructure framework, it is expected that the trapped electron feels the Coulomb repulsion force that pushes the electron away favoring its reaction with adsorbents. The overall effect results in providing charge reservoir sites which promote the interfacial charge transfer mechanism. Cement microstructure can therefore effectively mediate in TiO₂ photocatalytic performance.

5. Nano-TiO₂-cement composites preparation for photocatalytic applications

When preparing photocatalytic cement, it is crucial to take into account some key factors that will determine both the compound photodegradant capacity and its final performance as structural material. On the one hand, the choice of photocatalytic dosage and insertion method

usually depends upon the composition of the host cement-based composite. On the other hand, TiO_2 photocatalyst can be used either as freestanding particulate or as coating on a substrate. However, much more insight is needed from engineering design and modeling point of view, for successful application of the laboratory-scale techniques to large-scale operation. Questionless, there exist some beneficial effects on the environment derived from inclusion of TiO_2 nanoparticles to cement production. But on its own, cement is a highly efficient material in terms of energy consumption and welfare that generates; therefore we should aim to respect its identity in attempting to develop a more sustainable material.

5.1. Optimal content and inclusion method of nano- TiO_2 in cement

Initially, we focused on the optimum weight fraction of TiO_2 nanoparticles that should be added to the cement to develop a sufficiently efficient photocatalytic activity. Many works reported in literature ensure that the minimum fraction of nanoparticles to be added to cement in order to obtain a minimum photocatalytic activity must exceed 1% by mass of cement [16]. In fact, the photocatalytic properties begin to be significant from the eco-efficient point of view when the percentage of nanoparticles included in cement is close to 3%. This percentage not only provides photocatalytic activity to the material, but also favors the development of hydration products, leading to improvements of up to 62% in mechanical properties for long ages [17].

Regarding the preparation method, the TiO_2 nanoparticles can be synthesized by chemical-physical methods, such as sol-gel, using different precursors based on titanium oxides, such as titanium tetrabutoxide and titanium tetraisopropoxide (TTIP). These methods have proven to be suitable for the formation of spherical nanoparticles with controlled particle size. In addition, the so obtained nanostructured material features high specific area, which is an essential requirement to obtain adequate rates of photocatalysis.

At the end of the synthesis procedure, the nanoparticles can be kept in liquid medium or be subjected to a calcination process in order to increase their crystallinity and achieve a particulate system. Regardless, the most appropriate way to include the nanostructured TiO_2 in the cement matrix is found to be adding it directly to the hydration water. Thus, the nanoparticles will directly occupy the capillary pores that remain as the water is consumed due to the formation of products. In addition, the aqueous environment around the nanoparticles is guaranteed.

5.2. Suitable fabrication parameters of the cementitious matrix

Another key factor when preparing photocatalytic cement with adequate structural characteristics is the correct choice of manufacturing parameters for the cement mixture. Many researchers have used white cement to prepare their photocatalytic mixtures. The choice of white cement basically supports esthetic reasons, since from its preparation, it already seems a “clean” material and therefore more conducive to integration in a pollutant-free environment. In any case, other types of cement are also valid to form the cementitious matrix in which the nanoparticles are going to be housed. The requirement is so that the matrix must be properly hydrated and provide an adequate porous structure. In this sense, the water-cement ratio plays an extremely important factor.

The water-cement ratio directly influences the permeability properties of the material. Thus, a water-cement ratio of cement paste above 0.4 likely leads to having prohibitive sedimentation and bleeding. At the same time, the “Adsorb and Shuttle” (A&S) effect explained in previous sections implies that cement particles need to be kept in suspension before setting and hardening, in order to allow the adsorbents to be located in the microstructure. On the other hand, an excessive amount of cement would give rise to a material with significant hydration defects, since the available water would be almost entirely consumed, without leaving enough water molecules in the environment of the nanoparticles, in addition to a significant amount of clinker that would remain anhydrate.

Taking into account the previous comments as well as the experimental results reported in the literature, given that the water cement ratio is directly involved in the porosity of the resulting mixture, it seems essential to estimate what percentage of porosity will be in the cementitious matrix manufactured with a reasonable water-cement ratio. In this regard, 0.5 is the ratio most widely used in literature related to the manufacture of photocatalytic cements. Such water-cement ratio produces about 32.3% porosity in the cement matrix [18], along with a specific surface area of 134 m²/g and bulk density of 1448 kg/m³. These microstructural values have been used to predict the photocatalytic performance of nano-TiO₂-cement composites through a Monte Carlo approach [19], resulting in an increase of the amount and distribution of adsorbents within the exposed area. This likewise explains the effect of higher reaction rate constant obtained when 0.5 water-cement composite is present as the TiO₂ substrate.

6. Conclusions

This chapter concludes that the singularities and the qualities of the hydrated cement microstructure enhance the photocatalytic processes, driven by titanium dioxide, to create environment-friendly cement. We have exposed the microstructural characteristics of cement and those aspects that make possible the promotion of photocatalytic activity. The cement porosity and the nanostructure of the C-S-H have been identified as surface modifiers of nano-TiO₂ providing charge reservoir sites which promote the interfacial charge transfer mechanism. Cement microstructure can therefore effectively mediate in TiO₂ photocatalytic performance. Suggested directions have been provided for the preparation of photocatalytic mixtures, taking into account both the suitable content of nano-TiO₂ as well as the formulation of the cementitious material, according to the most recent trends reported. This framework is also a starting point for future studies that seek to improve the photocatalytic response of titanium dioxide inserted in the cement matrix as well as to provide implications for the application of photocatalytic cement technology in the construction materials industry.

Conflict of interest

The author declares that there was no conflict of interest.

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